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POLYDIMETHYLSILOXANE- POLYALKYLENEOXIDE BLOCK COPOLYMERS

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ABSTRACT

The synthesis of polydimethylsiloxane-polyalkyleneoxide block copolymers has been carried out in solution by hydrosilylation reaction of preformed α,ω -bis(dimethylhydrosilyl) polydimethylsiloxane (HcPDMS) oligomers to allyl end-capped polyalkyleneoxide (PAO), in the presence of Pt catalyst. The products were characterized by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectrometry, and gel permeation chromatography. The thermal stability was determined by thermogravimetric analysis.

Key Words: Block; Copolymer; Ethyleneoxide; Hydrosilylation; Polyalkyleneoxide; Polydimethylsiloxane; Propyleneoxide

INTRODUCTION

The polydimethylsiloxane-polyalkyleneoxide block copolymers have become of considerable interest for many technical applications from additives in polyurethanes to wetting agents in agrochemicals (1,2). They have excellent surface-active properties and can reduce the surface tension of water to lower values than normal hydrocarbon surfactants (3–6). They have good thermal stability, and, at the same time, they usually do not precipitate at low temperatures because the

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compounds cannot crystallize due to their highly branched structure. Also, due to their molecular structure, the adhesion forces between the individual molecules in interfacial films are small, and, for this reason, the compounds are good wetting agents; they are also excellent lubricants (7,8). Silicone surfactants are also known for their low physiological risk in cosmetic applications, because, due to their different structure, they cannot penetrate into normal lipid bilayers (9,10).

The molecular structures of polyalkyleneoxide modified silicones are typically classified into a branch-type, a triblock-type, and a comb-type and/or a pendant-type. The hydrophilic group is linked to the silicon atom with CH_2 groups making the Si-C link between the hydrophobic and the hydrophilic groups, or by -O- atom making the Si-O-C link between the siloxane alkylene-oxide groups (11).

The aim of this work was to prepare strictly controlled alternating polydimethylsiloxane-polyalkyleneoxide (PDMS-PAO) block copolymers containing Si-C linkages based on $(\text{CH}_2)_3$ intersegments by hydrosilylation reactions of allyl-terminated polyalkyleneoxide with α,ω -bis(hydrosilyl)poly-dimethylsiloxane (H_cPDMS) using a Pt catalyst (Scheme 2).

The synthesized PDMS-PAO block copolymers were characterized by gel permeation chromatography (GPC), thermogravimetric data (TGA), viscosity (η_{cst}^{25}), IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D_4) was supplied by Fluka AG with the following characteristics: b.p. = 175°C ; $n_{\text{D}}^{20} = 1.396$; $d_4^{20} = 0.955$; purity: 99% (GC). 1,3-bis(H)-tetramethyldisiloxane, supplied by ABCR GmbH and Company, with b.p. = $70.5\text{--}71^\circ\text{C}/731$ mm Hg, $n_{\text{D}}^{20} = 1.37$, and $d_4^{20} = 0.7572$.

Styrene-divinylbenzene copolymer with sulphonic groups (PUROLITE CT 175) was utilized after conditioning, which consisted of washing with water, washing with 4% NaOH solution, regeneration with a 4% HCl solution, washing with water, and subsequent dehydration by azeotrope distillation with toluene and vacuum drying (110°C , 20 mm Hg). The cation-exchanger had the following characteristics: active group, SO_3H ; volumic exchange capacity, 1.8 meq/mL; gravimetric exchange capacity, 4.2 meq/g; specific surface, $35\text{ m}^2/\text{g}$.

Montmorillonite K 10 (natural Aluminium silicate) from Fluka was used as received. Toluene was dried on molecular sieves and freshly distilled. Other solvents and reagents were high-grade commercial products used without further purification.

Measurements

The IR spectra were recorded on a Specord M-80 Carl Zeiss, Jena Spectrophotometer using KBr discs. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were performed



on a Bruker DRX 400 Spectrometer in CDCl_3 . Number-average molecular weights (M_n), weight-average molecular weights (M_w), and molecular weight distributions were determined by gel permeation chromatographic analyses (GPC) with a PL-EMD 950 evaporative mass detector instrument by using chloroform as eluant after calibration with standard polystyrene samples. Viscosimetric analysis in toluene was used to obtain viscosimetry average molecular weights (M_v).

Synthesis of HcPDMS

A difunctional H-Si-terminated polysiloxane oligomer HcPDMS was obtained by an equilibration reaction of D_4 and functionalized Si-H 1,1,3,3-tetramethyldisiloxane (TMDS) as end-capped (Scheme 1), in the presence of a 2–3% dried copolymer styrenedivinylbenzene sulfonic acid (PUROLITE CT 175) with an water content of 3% (w/v), as cationic polymerization catalyst under stirring for 21/2 h at 90°C (12). Cyclic compounds and unreacted chain stoppers were removed by distillation at 160°C and 20 mm Hg.

Using various D_4/TMDS molar ratios, different molecular weights of Si-H-terminated polydimethylsiloxane were obtained. The oligomer (purified by cyclic compounds and unreacted disiloxane) was characterized by end-group analysis (13), the determination of the molecular weights using GPC data (Fig. 4) and viscosimetric analysis (Table 1).

Synthesis of Allyl Terminated Polyalkyleneoxide Macromers

The α,ω -dialyl polyethyleneoxide with $M_n = 2000$ (PEO_{2000}) were prepared by the reaction of a mixture containing allyl alcohol and ethyleneoxide, in the presence of NaOH pellets in benzene, at 120°C for 5 h (14). The benzene was removed by distillation under vacuum (20 mm Hg) at 100°C . The functionalized polymer was neutralized with Montmorillonite. After filtration, the product was dried under high vacuum at 50°C .

The α -allyl, ω -hydroxy-poly(ethyleneoxide, propyleneoxide) copolymers (PEO-PPO_{2200}), were prepared by the reaction of a mixture containing allyl

Table 1. α,ω -Bis(dimethylhydrosilyl)polydimethylsiloxanes H_cPDMS

No.	H (%)	M_n^a	M_v^b	M_w^c	M_n^c	M_w/M_n	η^{25} (cSt)
1.	0.1309	1500	1300	1940	15	1.24	11
2.	0.0670	3000	1245	3440	1800	1.91	21
3.	0.363	6500	5432	5977	3762	1.58	59
4.	0.0171	12000	12700	20680	10500	1.97	108

^a M_n based on the endgroups data.

^b M_v calculated with relation: $\log \eta_{\text{cSt}}^{25} = 1.00 + 0.0123M^{0.5}$ cSt.

^c From GPC data.



Table 2. The Characteristics of Polyalkyleneoxides Macromers

No.	Unsaturated (mE/g)		OH (mg KOH/g)		M_n^a	M_w^b	M_n^b	M_w/M_n
	Calculated	Determined	Calculated	Determined				
PEO ₁	1.0	0.97	56.0	55.83	1030	2260	565	4.00
PEO ₂	0.50	0.5	0	0.012	2000	5518	3605	1.53
PEO-PPO	0.5	0.45	23.5	25.43	2200	6400	1855	3.45

^a M_n was calculated with the formula: $M_n = 1000/\text{unsaturated}$.

^b From GPC data.

alcohol, ethyleneoxide, and propyleneoxide, in the conditions described above, but only one of the copolymer ends was blocked with an allyl group.

The content of allyl groups was determined by the reaction with saturated mercuric acetate in methanol and the titration of acetic acid with 1 N KOH (15). The OH groups content was determined by esterification of OH groups with phthalic anhydride in pyridine at $115 \pm 2^\circ\text{C}$ and treatment of anhydride excess with NaOH 0.5 N.

For the diallyl-terminated polyalkyleneoxide (PEO₂₀₀₀), the low values of OH index (close to 0) indicates the absence of OH groups. For the PEO₁₀₀₀ and PEO-PPO₂₂₀₀, the determined values of unsaturation and OH groups indicate the presence of one allyl and one OH terminated group.

The molecular weights were determined from GPC data and by the unsaturated groups (Table 2).

Synthesis of Polydimethylsiloxane-Polalkyleneoxide Block Copolymers

A series of polydimethylsiloxane-polyalkyleneoxide (P₁-P₄) block copolymers type (AB)_n, where A = polydimethylsiloxane and B = polyethyleneoxide, were synthesized by hydrosilylation reactions of α,ω -diallyl polyethyleneoxide (PEO₂₀₀₀) macromers with Si-H-terminated PDMS in toluene, catalyzed by H₂PtCl₆ · 6H₂O, 2% (w/v) solution in isopropanol. The polyethyleneoxide was dehydrated by azeotropic distillation. The method is outlined as follows: 10 g (0.005 mol) polyethyleneoxide PEO₂₀₀₀ and 25 mL of dry toluene were charged in a 250-mL reaction flask fitted with stirrer, thermometer, Dean-Stark trap, condenser, and nitrogen inlet. The system was slowly heated to 120–125°C to remove the water-toluene azeotrope (20 vol.-%) and continuously purged with dry nitrogen. After cooling to ~90°C, 0.1 mL solution 2% H₂PtCl₆ · 6H₂O in anhydrous isopropanol was added. The system was reheated to 130°C and 15 g (0.005 mol) H_CPDMS ($M_n = 3000$) was added dropwise and stirred for 24 h. The complete conversion of Si-H groups to Si-C linkages is controlled by the IR spectra of the reaction mixture. Then, the toluene was removed by heating the reaction mixture under vacuum to yield crude copolymer.

The unincorporated siloxane was removed from the block copolymer by extraction with petroleum ether; the unreacted PEO was removed by extraction with



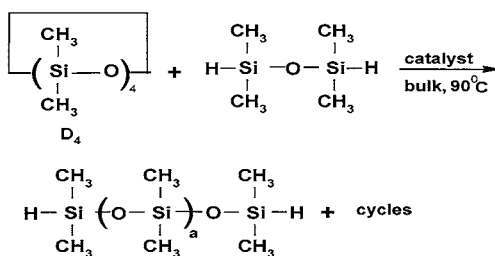
methanol. Finally, the purified product was dried in vacuum at 50°C for 20 h. The resulting product is a white–grey wax, soluble in several organic solvents. The polymers display a good hydrolytic stability. The characteristics of the synthesized block copolymer (P₂) are listed in Table 3.

The triblock copolymers PAO-PDMS-PAO (P₅–P₁₀) were obtained by hydrosilylation reactions of α -allyl, ω -hydroxy-polyethyleneoxide oligomer (PEO₁₀₀₀) or α -allyl, ω -hydroxy-poly(ethyleneoxide, propyleneoxide) copolymer (PEO-PPO₂₂₀₀) with H_cPDMS in toluene, in the presence of H₂PtCl₆ · 6H₂O as catalyst. For P₉ product the method is outlined as follows: into a 250-mL round-bottom flask, equipped with a thermometer, nitrogen gas inlet, mechanical stirrer, and dropping funnel, 18.8 g (0.0085 mol) of PEO-PPO₂₂₀₀ and 50 mL of toluene were placed. The mixture was heated, and 10 mL of toluene-water azeotrope was distilled.

The temperature of the system was adjusted to 90–100°C and 0.2 mL of 2% H₂PtCl₆ · 6H₂O was added. Then, the system was heated at 125–130°C and 2.1 g (0.0007 mol) Si–H terminated PDMS (*M_n* = 3000) were added through the funnel and stirred for 20 h. The complete conversion of Si–H groups is controlled by the IR spectra of the reaction mixture. The solvent was removed by heating the reaction mixture under vacuum to yield the copolymer. The unreacted silicone was extracted with petroleum ether (30–60°C). The obtained product (P₉) is a soluble polymer in the several organic solvents. The characteristics of the block copolymers are listed in Table 3.

RESULTS AND DISCUSSION

The precursor oligomers, H_cPDMS, were prepared by heterogeneous catalysis in the absence of solvents, as shown in Scheme 1. After reaching the equilibrium, the catalyst was separated by filtration and the volatile fraction (unreacted inferior cyclic compounds and, eventual, disiloxanes) was removed by vacuum distillation. The length of siloxane segments and the molecular weights of the siloxane precursors H_cPDMS were controlled by the D₄/TMDS ratio. The IR spectra indicates an absorption band at 2140 cm⁻¹ for Si–H groups and the band characteristic for the



Scheme 1.



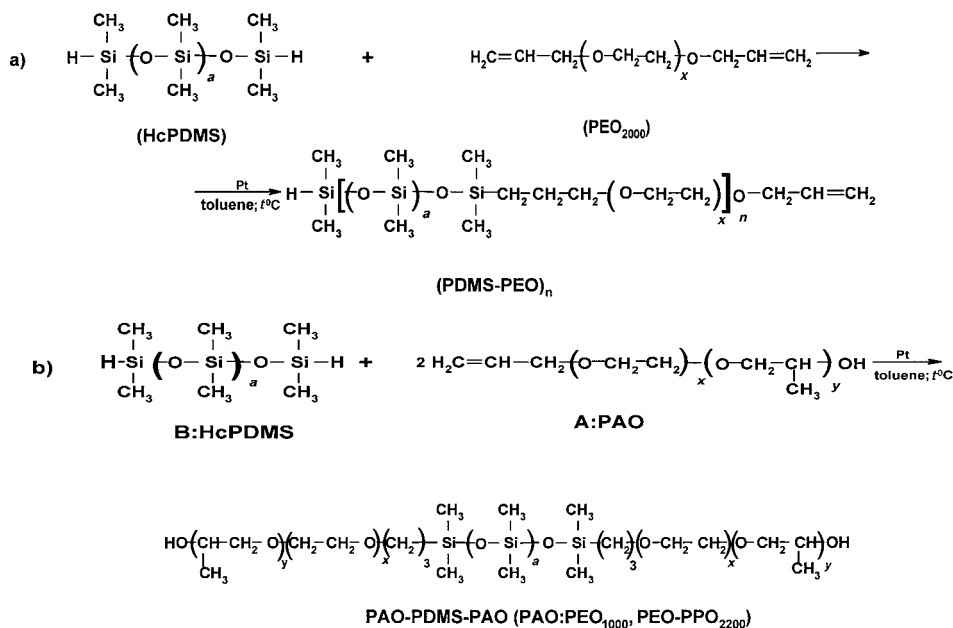
Table 3. The Characteristics of Block Copolymers PDMS-PAO

No.	The blocks		The Copolymer Type	PDMS ^a %mol	PEO ^a %mol	PPO ^a %mol	A/B	M _v ^b	M _w ^c	M _n ^c	M _w /M _n	The Aspect
	PDMS (B)	PAO (A)										
P1.	1500	2000	(AB) _n	32.30	66.85	—	1/1	10200	16074	9200	1.74	Cire
P2.	3000	2000	(AB) _n	53.33	46.66	—	1/1	13300	9769	5666	1.72	Cire
P3.	6500	2000	(AB) _n	68.15	31.84	—	1/1	18500	19217	8700	2.20	Cire
P4.	12000	2000	(AB) _n	82.75	17.24	—	1/1	45000	40426	26283	1.53	Cire
P5.	3000	1000	ABA	45.69	54.30	—	1/2	7900	18975	8250	2.30	Cire
P6.	6500	1000	ABA	57.12	42.87	—	1/2	14000	28222	10300	2.74	Cire
P7.	12000	1000	ABA	81.34	18.65	—	1/2	23500	57350	18500	3.10	Cire
P8.	1500	2200	ABA	18.50	45.50	37.00	1/2	9100	14150	4982	2.84	Liquid visq.
P9.	3000	2200	ABA	23.60	42.70	34.00	1/2	18400	20310	8220	2.47	Liquid visq.
P10.	6500	2200	ABA	42.80	31.00	26.00	1/2	26000	31530	10870	2.90	Liquid visq.

^aThe composition was determined by ¹H-NMR spectra.

^bM_v was calculated with formula: $[\eta] = 8.28 \times 10^{-3} \times M^{0.72}$.

^cM_w end M_n was determined by GPC.

Scheme 2.

siloxane bond ($1000\text{--}1100\text{ cm}^{-1}$), which is specific for the chains with multiple siloxane units. The average molecular weight M_n of the siloxane oligomers was determined by GPC and Si-H end groups analysis (Table 1).

The polyalkyleneoxide macromers with α,ω -allyl, or α -allyl, ω -hydroxy end-capped were synthesized by copolymerization reaction in the presence of KOH catalyst. After purification, this polymers were characterized by IR spectra, indicating characteristic absorbtions for $-\text{CH}_2\text{--O--CH}_2-$ (940 cm^{-1} , $1070\text{--}1150\text{ cm}^{-1}$), $-\text{CH}=\text{CH}_2$ (16 cm^{-1}), $-\text{OH}$ ($3600\text{--}3640\text{ cm}^{-1}$), as shown in Figure 1. The molcular weights were determined (Table 2) from the allyl groups analysis and GPC data. The synthesis of polydimethylsiloxane-polyethyleneoxide block copolymers (AB)_n was carried out at a 1:1 molar ratio of diallyl end-capped PEO and Si-H terminated PDMS, by hydrosilylation. The synthesis of PAO-PDMS-PAO block copolymers type ABA, where A:PAO (PEO₁₀₀₀ or PEO-PPO₂₂₀₀) and B:PDMS were carried out at a 2:1 ratio of allyl-PAO-OH and H_cPDMS (Scheme 2).

The IR spectra of PDMS-PAO block copolymers indicates the conversion of Si-H end groups by the complete disappearance of the 2140 cm^{-1} absorption band characteristic of the Si-H-terminated PDMS and the appearance of Si-CH₂- linkages at $1220\text{--}1200\text{ cm}^{-1}$ and of a large absorption band at $1000\text{--}1100\text{ cm}^{-1}$ for the Si-O-Si linkages, which is not present in the PAO spectra (Fig. 1).

¹H-NMR analysis was used to determine the composition and relative block size of the block copolymers $\delta = 0.13\text{ ppm}$, propyleneoxide proton at $\delta = 1.15\text{ ppm}$



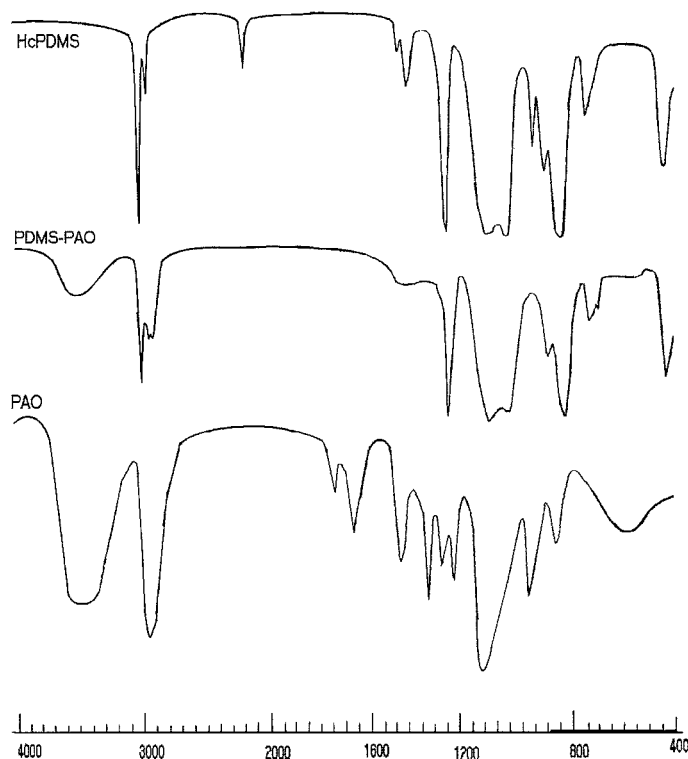


Figure 1. IR spectra of H_cPDMS(2), PAO(PEO-PPO) and PDMS-PAO(P₉).

and ethyleneoxide proton from the PAO segment at $\delta = 3.8$ ppm (Fig. 2). The proton signal $-\text{CH}_2-$ from $\text{Si}-(\text{CH}_2)_3$ linkage at $\delta = 0.35$ ppm, observed in the $^1\text{H-NMR}$ spectrum, is in accordance with a structure containing Si-C linkage between the PDMS and PAO blocks. The expected $(\text{AB})_n$ structure was also confirmed by $^1\text{H-NMR}$ spectra.

The $^{13}\text{C-NMR}$ spectrum of PDMS-PAO block copolymers is shown in the Figure 3, and it was used to identify the peaks of the carbon atoms in the methylene groups of the $\text{Si}-\text{CH}_2-\text{CH}_2-$ linkages (b, g) and the methylene groups of the ethyleneoxide and the propyleneoxide sequences (c, e).

The molecular weights and molecular weight distributions of the precursors and block copolymers PDMS-PAO were investigated by GPC. The results provided the formation of block copolymers (Table 3). The molecular weights are higher than those of the precursor oligomers but not enough high, especially for the $(\text{AB})_n$ block copolymers. This might be explained as a consequence of the heterogeneity of the precursor oligomers and block copolymers obtained by synthetic route. Molecular weight distributions were found to be monomodal, and not bimodal as might be expected for a mixture of the two oligomers (Fig. 4).



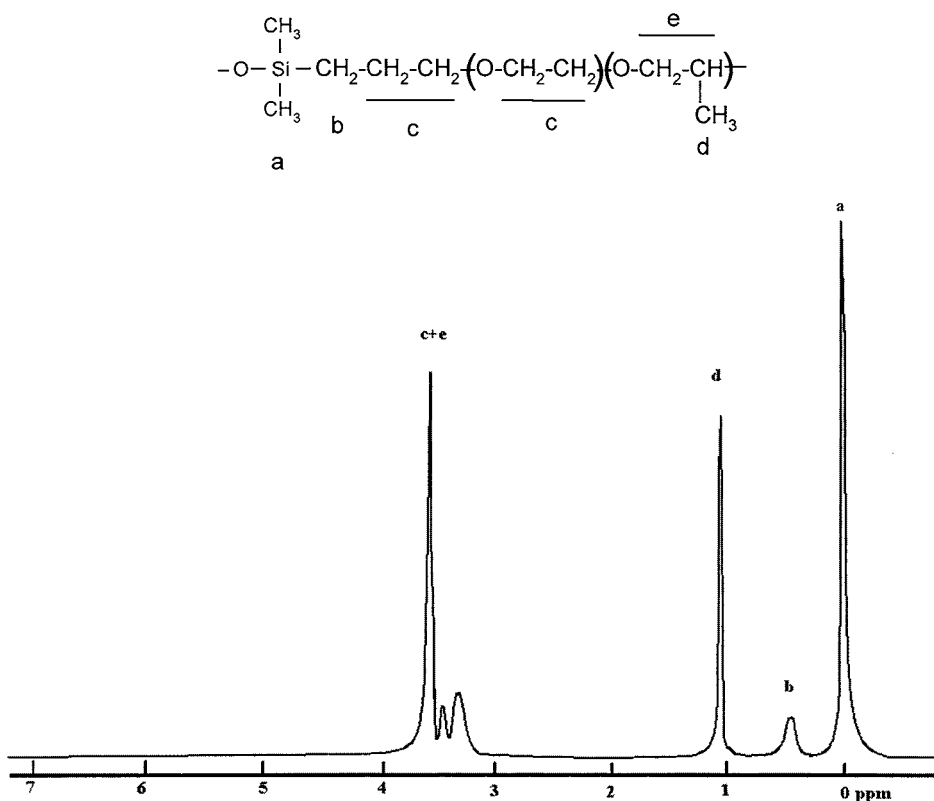


Figure 2. ¹H-NMR spectrum of PDMS-PAO(P₉).

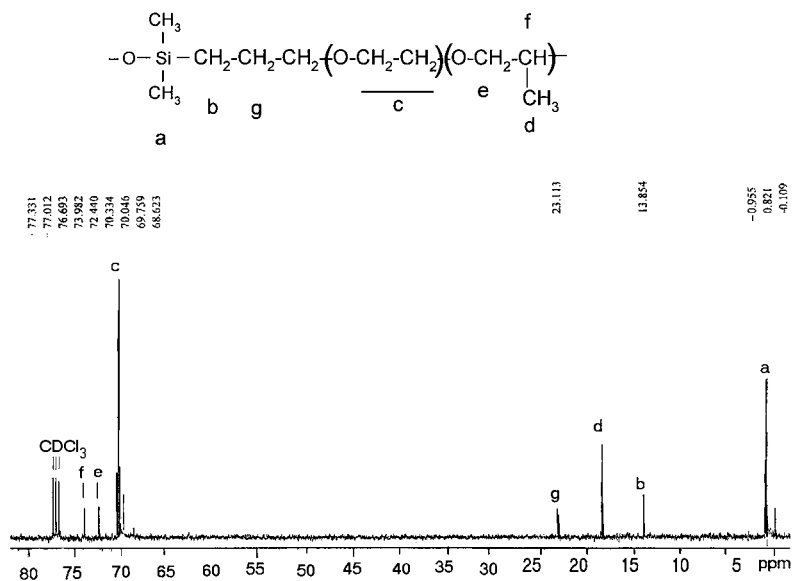


Figure 3. ¹³C-NMR spectrum of PDMS-PAO(P₉) in CDCl₃.



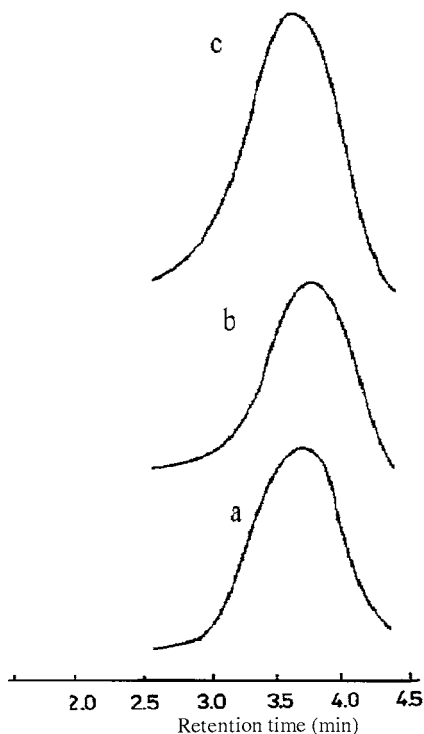


Figure 4. GPC data for: a) H_cPDMS; b) PAO; and c) PDMS-PAO (P₉).

The thermal stability of PDMS-PAO block copolymers was studied by thermogravimetric (TGA) and differential thermal (DTA) analysis. The samples were heated with a constant temperature rate of 12°C/min in air. The initial decomposition temperatures and the percent weight loss were determined from original thermograms and tabulated in Table 4.

Table 4. Block Copolymers PDMS-PAO TGA Analysis

No.	IDT (°C)	The Temperature (°C) of Thermique Decomposition (%)				
		10%	20%	30%	40%	50%
P ₁	47	122	194	240	280	322
P ₂	61	115	180	235	281	315
P ₃	85	218	277	352	430	469
P ₄	93	250	372	408	427	439
P ₅	41	143	205	300	385	420
P ₆	36	151	218	309	388	444
P ₇	70	354	411	432	454	471
P ₈	101	195	243	280	340	395
P ₉	115	207	252	295	347	400
P ₁₀	138	214	267	319	368	422



CONCLUSION

PDMS-PAO block copolymers were prepared by hydrosilylation reactions of allyl end-capped PAO with Si-H-terminated PDMS in toluene catalysed by a $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ solution in isopropanol. The products obtained were characterized by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and GPC analysis. The TGA data indicate a better thermal stability for the synthesized block copolymers.

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REFERENCES

1. Gruning, B.; Koerner, G. *Tenside Surf. Det.* **1989**, 26, 312; Schmidt, G. *Tenside Surf. Det.* **1990**, 27, 324; Schaefer, D. *Tenside Surf. Det.* **1990**, 27, 154.
2. Zhang, X.D.; Macosko, C.W. *J. Colloid Interface Sci.* **1999**, 215 (2), 270–279.
3. Giurgiu, D.; Hamciuc, V.; Ionescu, C. Patent Romania nr. 97327, Cl C 08 G 22/44, 1988.
4. Haesslin, H.W. *Makromol. Chem.* **1985**, 186, 357.
5. Kanner, B.; Prokai, B.; Eschbach, C.S.; Murphy, G.I. *J. Cell. Plast. Nov/Dec* **1979**, 315.
6. Jozik U.; Wolf, B.A. *Macromolecules* **1997**, 30, 4713.
7. Noll, W.; Steinbach, H. *J. Polym. Sci.* **1971**, 34, 123.
8. Schwartz, E.G.; Reid, W.G. *Ind. Eng. Chem., Int. Ed.* **1964**, 56, 26.
9. Vick Steven, C. *Soop/Cosmetics/Chemical Specialties*, May 1984.
10. Iwanaga, T.; Shiogai, Y.; Kunieda, H. *Progr. Colloid Polym. Sci.* **1998**, 110, 225–229.
11. Sturmer, A.; Thunig, C.; Hoffmann, H.; Gruning, B. *Tenside Surf. Det.* **1994**, 31 (2), 90.
12. Schindler, S.; Rühlmann, K. *Plaste und Kautschuk* **1978**, 25 (7), 384.
13. Smith, L.A., Ed. *The Analytical Chemistry of Silicones*; New York: John Wiley and Sons Inc., 1991; 197.
14. Ionescu, M.; Dumitriu, V.; Mihalache, I.; Mihail, S. Unpublished results.
15. Smith, L.A., Ed. *Analysis of Silicones*; New York: John Wiley and Sons, Inc., 1974; 153.

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